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14. ABSTRACT Abstract This document reports the results of exploratory studies of technology for building devices to store electrical energy. The studies show that both volumetric (Wh/liter) and gravimetric (Wh/kg) energy densities of these novel devices can exceed those of best lithium-ion electro-chemical batteries. The new devices also have much lower internal energy dissipation. A significant advantage of these new devices is that they can be charged and discharged					
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Report Title

Prototyping Energy Storage Components for Hybrid Power Source

ABSTRACT

Abstract

This document reports the results of exploratory studies of technology for building devices to store electrical energy. The studies show that both volumetric (Wh/liter) and gravimetric (Wh/kg) energy densities of these novel devices can exceed those of best lithium-ion electro-chemical batteries. The new devices also have much lower internal energy dissipation. A significant advantage of these new devices is that they can be charged and discharged at about a three orders of magnitude faster rate than electrochemical devices such as batteries and electro-chemical super capacitors. This fast rate results because these devices are electronic in nature and they do not involve any slow chemical reactions or ion transport during their operations. This fast rate also means that the new devices have proportionally higher power density. In addition, these devices are expected to have much longer life time and to be less influenced by ambient temperatures. Fabrication of the new device is inexpensive and does not involve any toxic materials. The operation of the new device is safe and cannot result in explosive damaging as may occur with lithium-ion batteries.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. Gervasio, D. et al. 2009. "Next Generation Energy Storage Device," Quarterly Progress Report, Ft. Huachuca, Dec. 04, 2009.

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Palusinski, O. A., and D. Gervasio. 2007. "High Energy Density Storage Component for Hybrid Power Sources," Progress in Advanced Energy Conversion, ARO Workshop, Chapel Hill, September 6-7, 2007.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 1

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Matthew R. Powell	0.90
FTE Equivalent:	0.90
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Olgierd A. Palusinski	0.10	No
FTE Equivalent:	0.10	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
None	0.00
FTE Equivalent:	0.00
Total Number:	1

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Matthew R. Powell
Total Number:

Names of personnel receiving PhDs

<u>NAME</u>

None

Total Number:	1
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Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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None	0.00	No
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FTE Equivalent:	0.00
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Total Number:	1
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Sub Contractors (DD882)

Inventions (DD882)

Prototyping Energy Storage Components for Hybrid Power Source

Final Report

Proposal 53323CHII Period from June 21, 2007 to March 20, 2009

O. A. Palusinski, D. F. Gervadsio, Univ. of Arizona, Tucson

Abstract

This document reports the results of exploratory studies of technology for building devices to store electrical energy. The studies show that both volumetric (*Wh/liter*) and gravimetric (*Wh/kg*) energy densities of these novel devices can exceed those of best lithium-ion electrochemical batteries. The new devices also have much lower internal energy dissipation. A significant advantage of these new devices is that they can be charged and discharged at about a three orders of magnitude faster rate than electrochemical devices such as batteries and electrochemical super capacitors. This fast rate results because these devices are electronic in nature and they do not involve any slow chemical reactions or ion transport during their operations. This fast rate also means that the new devices have proportionally higher power density. In addition, these devices are expected to have much longer life time and to be less influenced by ambient temperatures. Fabrication of the new device is inexpensive and does not involve any toxic materials. The operation of the new device is safe and cannot result in explosive damaging as may occur with lithium-ion batteries.

Introduction

The aim of this project is to gain insight into the effects of nanoscale metal-dielectric structures on charge storage capability. The charge storage is created in a device built by electroplating metals into nanoporous dielectric membranes. The goal is to determine if we can use this approach to build capacitor devices with energy density close to or exceeding that of contemporary batteries. Anticipated advantages with this device are substantially lower internal energy dissipation (both in charging process and especially in the discharging process) and much higher rates of charging and particularly discharging than that of batteries. The higher discharge rate of the capacitor device makes it better suited than a battery as the primary source for pulse power applications, like periodical radio transmission.

Approach

Dielectric membranes are templates for building the capacitor type device. Basic structures are formed from suitable nanoporous ceramic (anodized aluminum oxide – AAO) and polymer (polycarbonate - PC, polyethylene terephthalate - PET) membranes. Metal inclusions are electroplated in the pores of membranes to form digitated energy storage devices (DESDs) or as

we recently call them, Nanostructure Ultra Capacitors (NUCs) to distinguish these devices from electrochemical devices like batteries and electrochemical supercapacitors. Technology for electroplating is well developed and well controlled. The membrane has a planar metal conductor formed on the lower side, which is used as a cathode in electroplating. Metal is then electroplated in the pores to fill $\frac{3}{4}$ of pore length with nanowires, which leaves an air gap between the metal nanowires and the top of the pores in the membrane. Subsequently an upper electrode is formed by physical vapor deposition of metal, which leaves a vacuum gap between the tips of the rods and the top electrode, or by spin or dip or spray coating. The resulting structure is schematically shown in Fig. 1a.

Major experiments to date were performed using $60[\mu m]$ thick alumina (Al_2O_3) membranes with pores of various diameters. These types of membranes are commercially available and have nominal pore of diameters of $20[nm]$, $100[nm]$, and $200[nm]$ respectively. An SEM image of a membrane with pores of $100[nm]$ diameter is shown in the Fig. 1b.

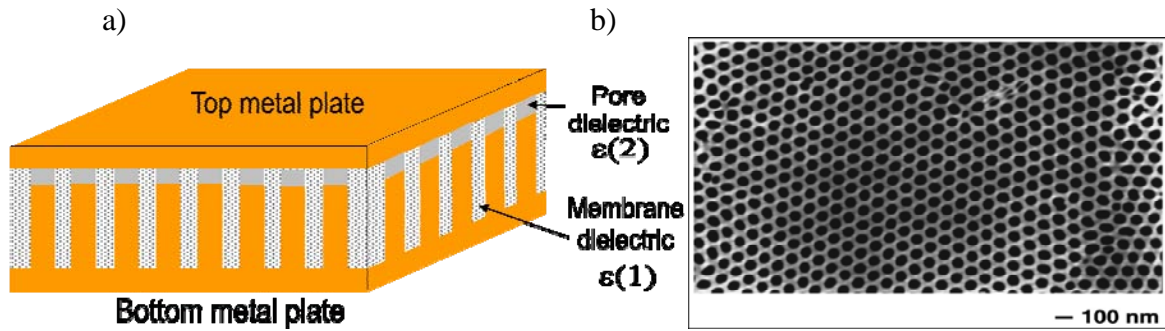


Fig. 1. Elements of NUC technology: a) sketch of structure, b) SEM image of membrane.

The alumina membranes can be easily and inexpensively fabricated via anodization of aluminum foil. The pores are formed by self-assembly via pitting and reprecipitation of metal oxide.

Motivation

The work is motivated by the need for low-weight high-speed electrical power supplies. Additional advantages in comparison to the batteries are: faster charging, lower internal energy dissipation, longer life time as measured by charge/discharge cycling, simpler control of charging and less restriction on discharge speed.

The NUC storage devices would serve as battery replacements in portable electronics and - with further development of device arrays - would serve in automotive and avionics applications. Another important use of our technology will be as the energy storage component in hybrid micro-power source systems in wireless networks for powering stand-alone sensors, actuators or radio transmitters working in periodic stand-by and active modes. The hybrid device would store energy during stand-by mode and would provide “pulse power” during an active mode, when a burst of power is needed, e.g., for wireless communication. Examples of hybrid micro-power systems are microbial fuel-cell + energy storage device or small battery + energy storage device

or photovoltaic solar cell + energy storage. Our energy storage device enables pulse power operation with microbial fuel cells and small batteries. Another advantage in case of battery + energy storage device is the reduction of internal dissipation in battery, which extends the battery life and enables use of smaller and lighter batteries.

Studies of Template Digitated Energy Storage Devices at the UC Irvine, CA

Research was conducted at the UC Irvine in the Department of Physics and Astronomy by Matthew R. Powell [2009], MS student working under supervision of Dr. Z. Siwy, faculty of the Department. A very small fraction of the device was numerically analyzed using a general canned multiphysics program called, COMSOL [2008]. The calculated electrical potential in a small section of the device is represented in the Figure 2.

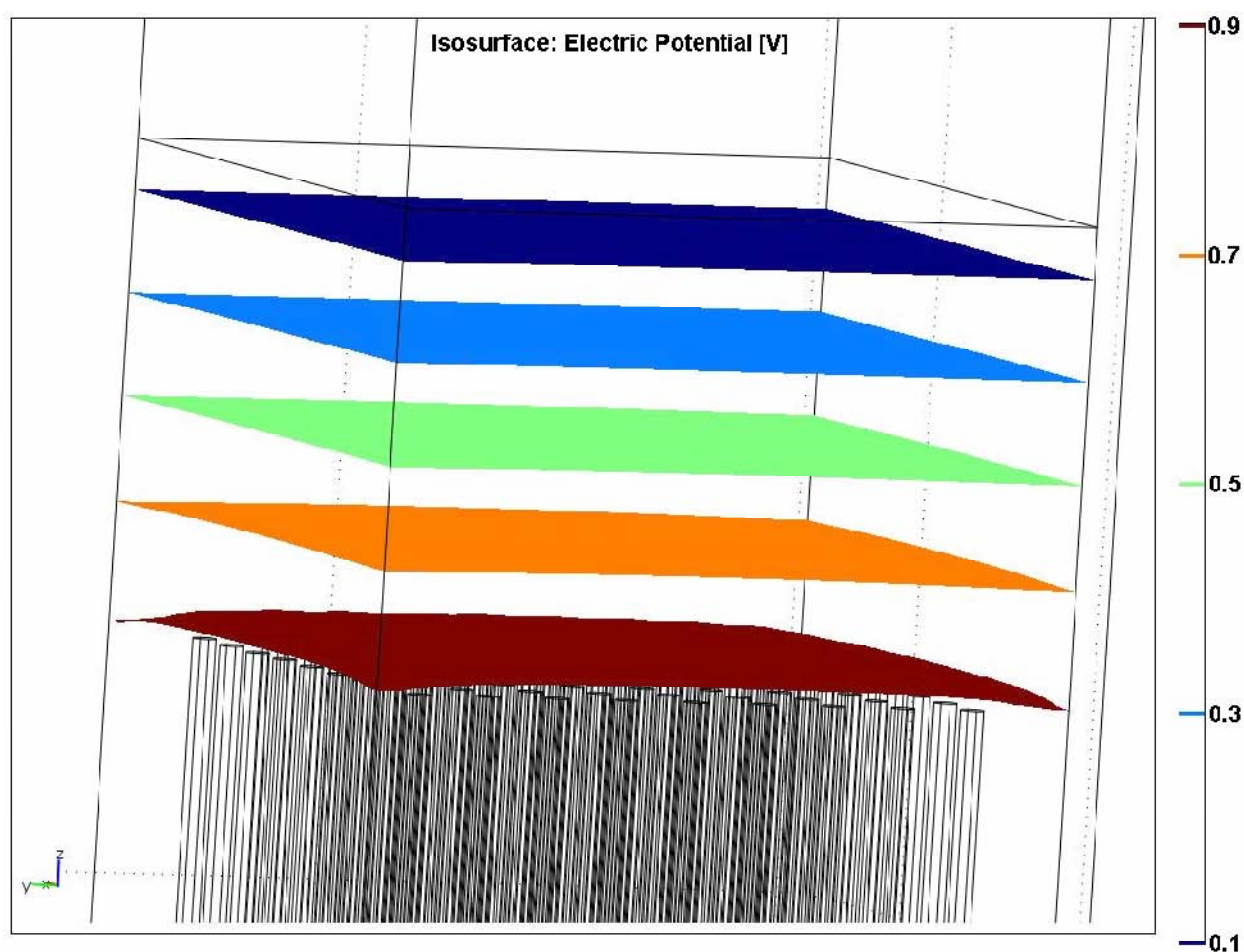


Figure 2. Equipotential Surface Levels generated by the program COMSOL; the potential levels are flat and parallel and a little edging effect is observed.

The program generated graphics showing that the equi-potential levels are flat and parallel to each other. The graphics show a little effect of rod edges or curvature of metal/dielectric interfaces. The assumption was made that the results can be expanded to the full area of the device. Conclusion drawn from this simulation is that the device structure can be represented by two parallel plates: one corresponding to the upper physical plate and the other being artificial, located at the tips of the metal rods (Figure 2). Experiments in building the storage devices were performed using track- etched PET membranes. These are fabricated by etching of the PET membranes, which were previously irradiated by energetic heavy ions. The irradiation yielded 10^7 to 10^9 tracks per cm^2 in the membrane. The etching was done at 70°C using sodium hydroxide (NaOH) of 0.5 M concentration. The process yielded a porous membrane with cylindrical pores. A fragment of the top of the membrane is imaged in the Figure 3.

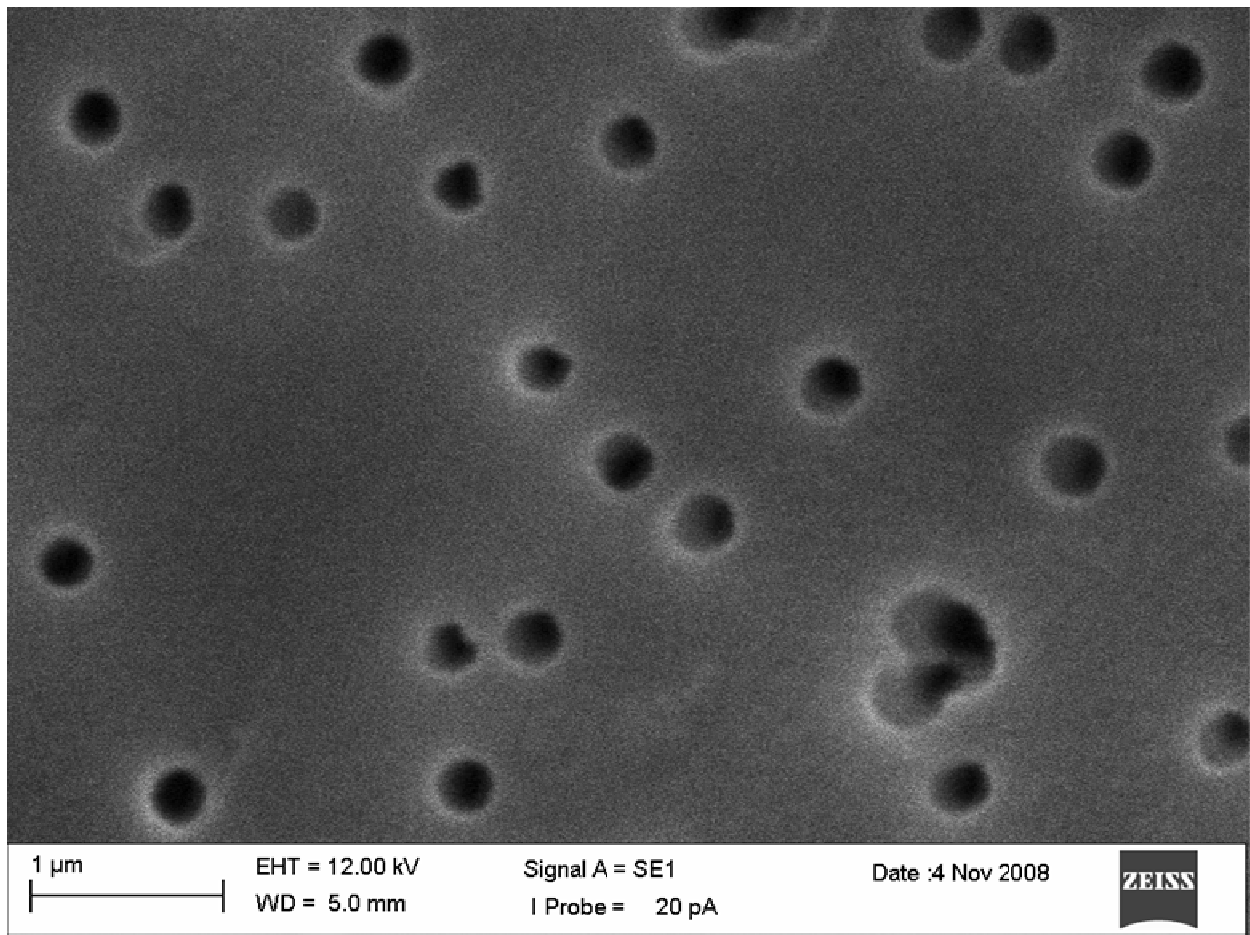


Figure 3. Top view of a fragment of PET membrane after etching.

A significant irregularity of pore distribution, due to almost random irradiation, is clearly visible. This randomness is not critical in building operational/working storage devices, but leads to low

pore density which certainly is detrimental in terms of device performance metrics such as volumetric energy density or gravimetric energy density.

A commercial alumina (Al_2O_3) membrane (available from Whatman [2009] with pores of 200 nm diameter) was also used in the laboratory for experiments. An SEM image of a fragment of the alumina membrane top surface is shown in the Figure 4.

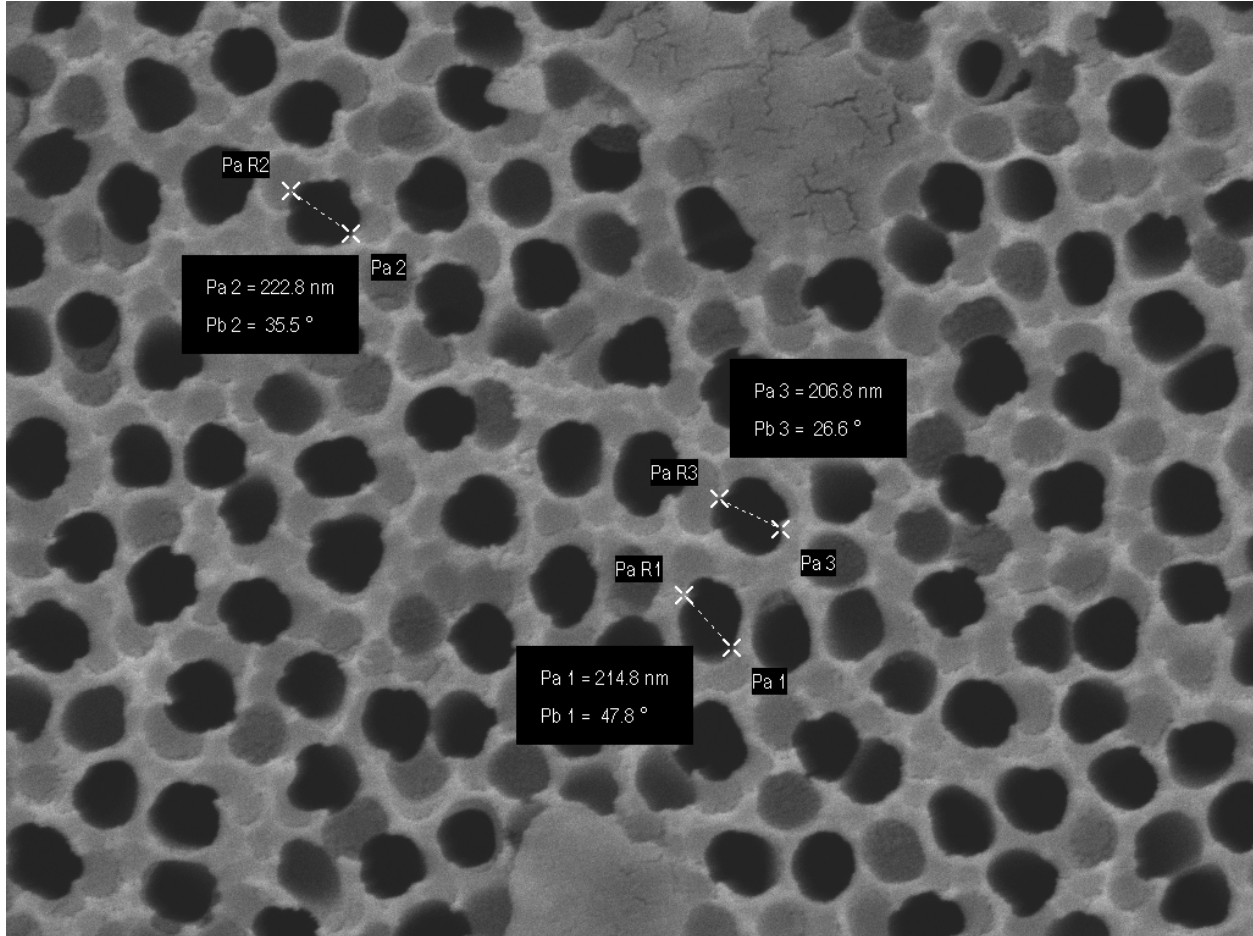


Figure 4. SEM image of a fragment of top surface of a Whatman Anodisk with pores of a nominal diameter of 200 nm.

The image shows some irregularity of pore distribution, but the randomness is obviously much smaller than in the PET membrane. The image shows some randomness in the pore diameter and shape. It should be noted that in the anodization of aluminum foil there are available good selections of chemistry, temperature, electrical bias, preliminary surface preparation, that would allow for better control of regularity in pores' diameter, shape, and pitch. Consequently, membranes with regular pores can be fabricated. Such results have been demonstrated in the literature.

In the laboratory experiment, conducted at the University of California, Irvine, it was found that the devices show a large capacitance shortly after fabrication. The hypothesis is that this is due to the moisture present in the structure after electroplating. When the device contains moisture the structure may behave like an electrolytic capacitor and thus the capacitance is large. The capacitance measured in the devices several days after fabrication was lower because of suspected evaporation of moisture. When the device is dry, then using the results of numerical simulation performed with the of the program COMSOL showed that, the capacitance can be crudely approximated by two parallel plates: one plate located at the end of the wires and the other plate physically formed on the top of the membrane, i. e., the opposite side of the insulating gap. The numerical model of the device, based on classical electrostatics, and solved numerically by the general solver COMSOL gives only a six fold increase in device capacitance. This, according to the thesis of the author, appears to be a result of effectively shortening the separation distance by a factor of six. This argument is rather strange, as according to the description of experimental work, the so called “shortening” of the separation distance would be very small – from 60 micrometers to 55 micrometers when 5 micrometer long wires were formed, as illustrated in the Figure 6. In addition, the thesis report does not present any numerical/experimental studies of solution convergence. The geometry of devices is very difficult to handle numerically, and a solution with a general canned program like COMSOL may yield the results that strongly depend on the selection of grid and control parameters of the program. Consequently, the numerical solutions require further carefully planned testing for the convergence and accuracy.

The experimental results of electroplating copper and gold in the pores of commercial alumina membranes of 200 nm diameter are shown in the Figures 5 and 6 respectively.

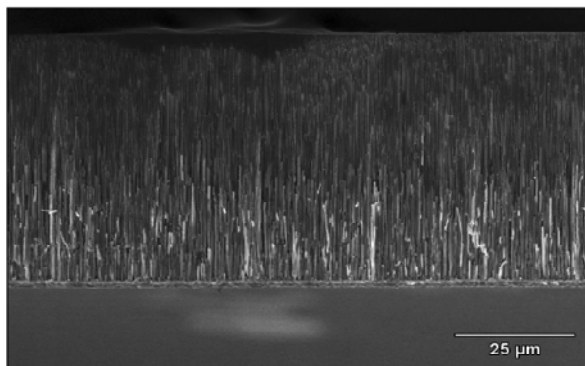


Figure 5. SEM image of copper nano-wires electroplated in the pores of alumina membrane.

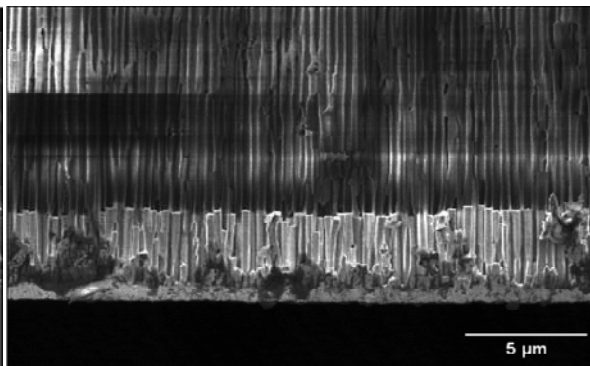


Figure 6. SEM image of gold nano-wires electroplated in the pores of alumina membrane.

The copper plating shown by the image depicted in the Figure 5 reveals very irregular filling of pores. There is not any speculation about a reason (or reasons) for this irregularity. More experiments should be performed to find the cause of the observed irregularity and determine possible remedies by hardware and control parameters of plating process.

The gold plating gives rather regular fill of pores as illustrated by the SEM image enclosed here as the Figure 6. Further analysis of the process yielding the structure shown in Figure 6 may give some information how to improve the copper plating.

Studies at the University of Arizona (UA) and Arizona State University (ASU)

This section reports more recent studies conducted in Arizona supported by other funds [Gervasio and Palusinski 2008]. This section is written to provide a contrast to the results obtained at the UC Irvine and to show that a continuation of research and development of NUC technology is worthwhile [Palusinski and Gervasio 2007, Palusinski et al. 2007]. The performance of devices is much better and indicates significant potential of the investigated technology for competing with other storage technologies such as electro-chemical batteries or electro-chemical super capacitors. For example, the achieved gravimetric capacitance densities in the prototypes, which were independently fabricated (by the teams of Palusinski at UA and Gervasio while at ASU) in alumina membranes with pores with diameter of 200[nm], show that

the NUC devices have an average capacitance of $C_{meas/grav} = 2.7 \left[\frac{mF}{gram} \right]$.

NUC performance can be expressed in terms of volumetric or gravimetric energy densities, which are given in the units of $[W \cdot h / liter]$ or $[W \cdot h / kg]$ respectively. These metrics are calculated [Palusinski 2009] from the capacitance densities multiplied by the square of nominal voltage, which is limited by the dielectric strength of the gap between the top and bottom electrodes. Prototypes were built by filling the pores up to 75% of length (60[μm]) leaving a 15[μm] gap between the nanowire tips connected to the bottom electrode and bottom of the flat upper electrode. When upper electrode is formed by physical vapor deposition there is a vacuum in the gaps, and thus the dielectric strength is controlled by the behavior of alumina.

Because the dielectric strength is determined by the alumina, which is $E_{bkAAO} = 1.6 \cdot 10^5 \left[\frac{V}{cm} \right]$,

and for the 15[μm] distance from the upper electrode, this dictates the breakdown voltage of 250[V]. Assuming a safe voltage of 150[V], the metrics for the prototypes are given in the first row of the table of energy densities using bold fonts.

Pore diameter [nm]	Volumetric density $\left[\frac{W \cdot h}{liter} \right]$	Gravimetric density $\left[\frac{W \cdot h}{kg} \right]$
200	33.6	6.83
100	134	27.4
20	3,361	683

The last two rows give metrics calculated using modeling. Note: These calculations predict energy densities of NUC which can exceed that of the best Li-ion batteries.

Very recent experiments reported in a recent report [Gervasio et al. 2009] confirm the trend predicted by the above table. However the nominal diameters of acquired commercial membranes are not what were expected as shown in the table below.

Nominal Pore Width (nm)	Pore Width From SEM (nm)
20	187
100	230
200	247

In the above table, the nominal pore diameters are given along with the actual pore diameters as determined by scanning electron microscopy (SEM).

Furthermore the SEM images of the nanowires in the membranes showed that the diameters of the wires that were grown in the pores matched neither the nominal nor SEM determined pore diameters. The wire diameters were 187, 230 and 247 nm when grown in the membranes that were nominally 20, 100 and 200nm in pore diameter, respectively.

The capacitances were measured for NUC's made in commercial membranes (from the same batch) with pores that were nominally 20, 100 and 200 nm in diameter. The capacitance and mass of these NUCs are given as a function of the nominal pore diameter in Figure 7.

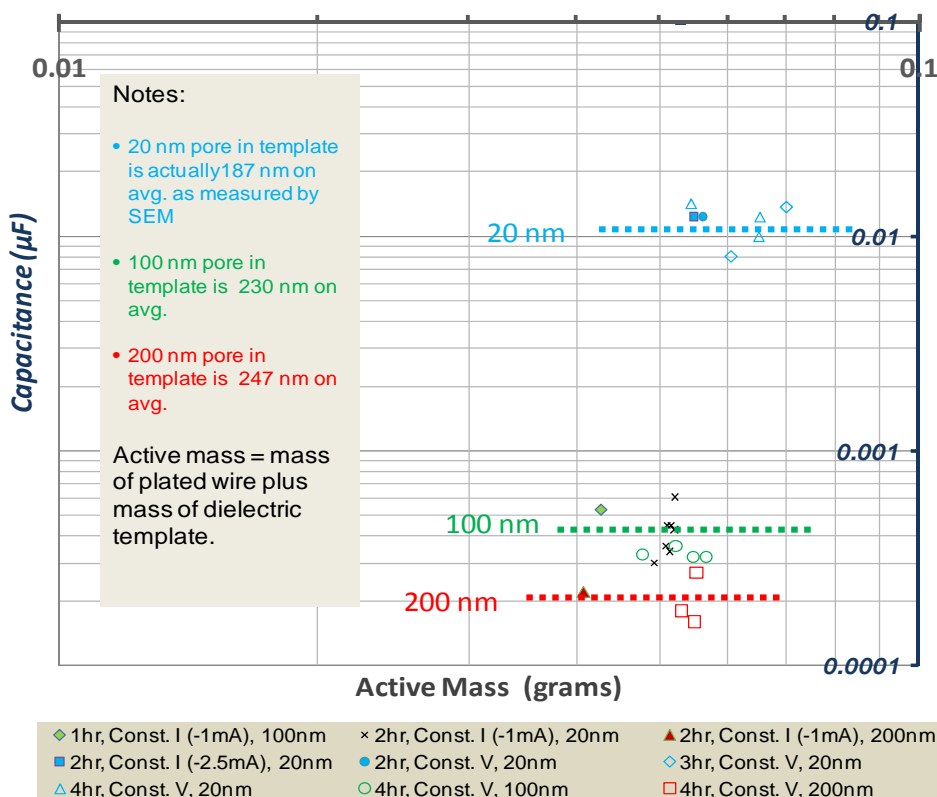


Figure 7. Capacitance as a function of wire diameter and measured active mass.

The measured capacitance and measured volumes of these NUCs are given as a function of the nominal pore diameter in Figure 8.

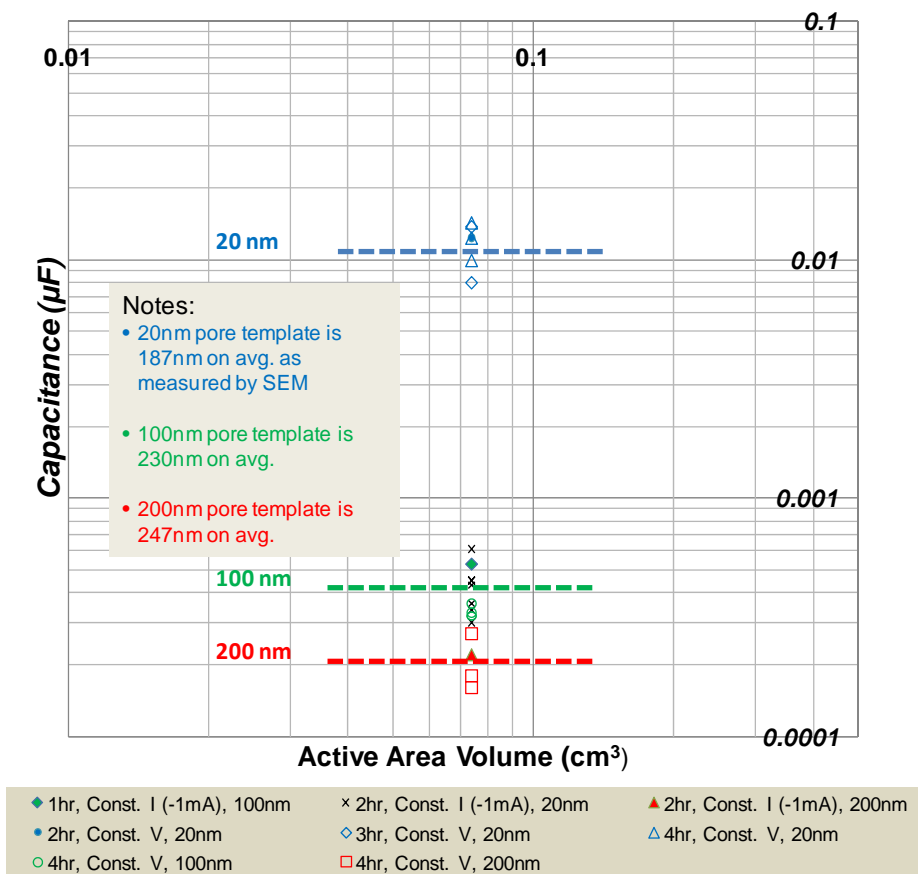


Figure 8. Capacitance as a function of wire diameter and measured active volumes.

For better illustration of interesting trend in the gravimetric and volumetric capacitance densities of the devices the data in Figures 7 and 8 are also represented in Figures 9 and 10 in different scales.

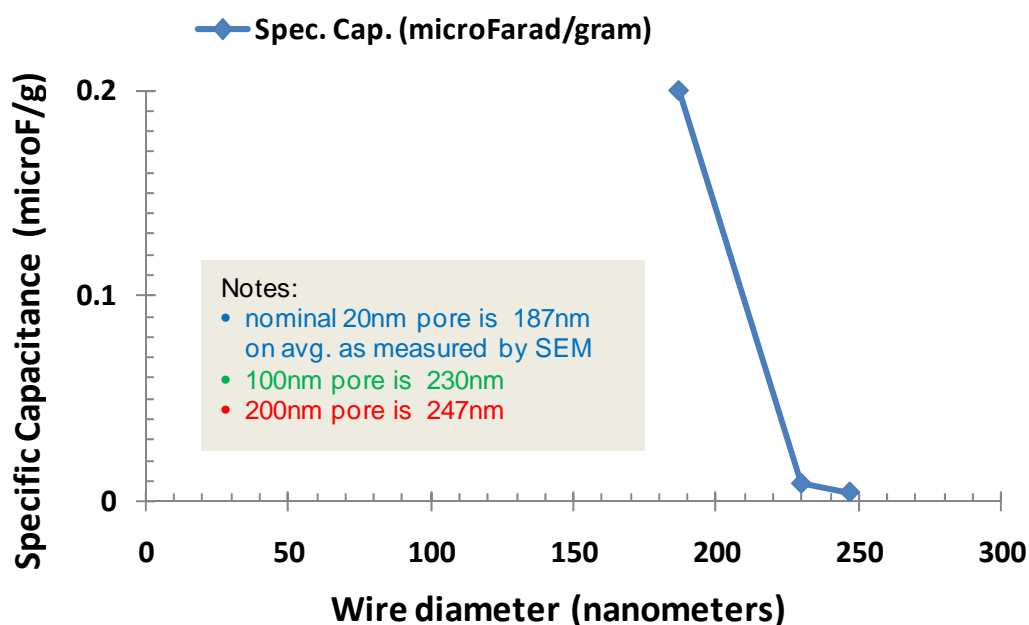


Figure 9. Specific Capacitance as a function of wire diameter

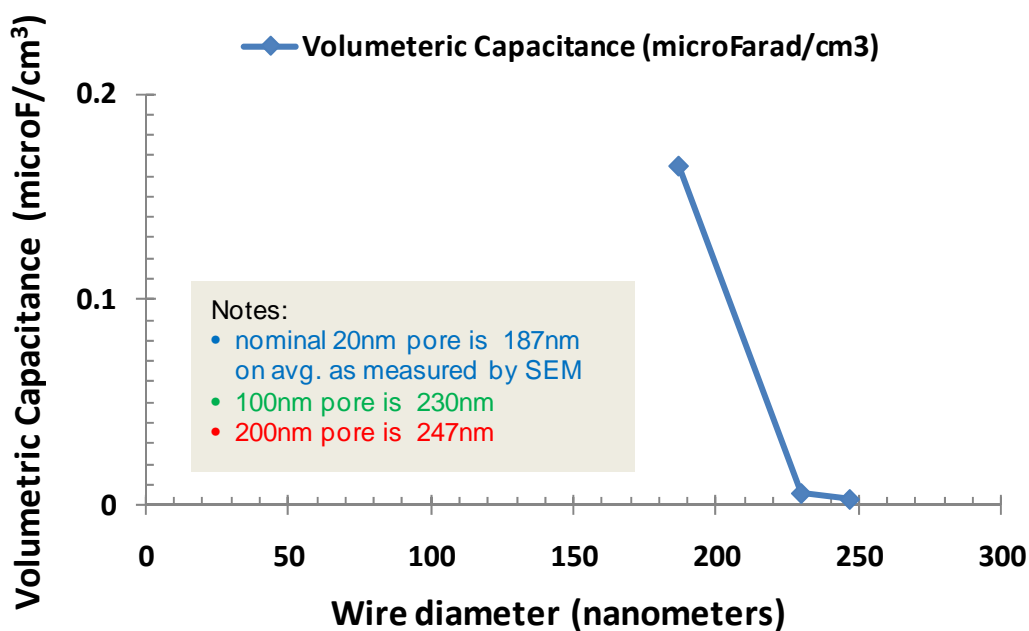


Figure 10. Volumetric Capacitance as a function of wire diameter

The results of Figure 7 to 10 are presently considered qualitative, since the pore diameters are so different than the nominal pore diameters. Nonetheless, the trend is clear that the capacitance per unit mass or volume increases when the diameter of the nanowires in the membrane decreases.

Conclusions

NUC's have several advantages over chemical batteries:

- store directly electrical energy with high energy efficiency

chemical batteries convert energy, portion of energy is lost internally in conversion during charging and discharging

- fast charge/discharge with low internal power dissipation

current carriers are electrons ~ 1000 times faster than ions in batteries

- longer life time (no chemistry, no chemical wear out)

- high volumetric and gravimetric energy density

- negligible self-discharge

batteries & electrochemical supercapacitors require trickle-charge to maintain charge

- no problems with overcharging – control circuitry is not required

- no problem with overheating or explosions

NUC's are fabricated by electroplating in nano-porous substrates

- substrates are commercially available, inexpensive

Electroplating has significant manufacturing advantages

- well known and well controlled process
- low processing energy
- low cost of fabrication
- no toxic wastes in manufacturing or disposal

NUC's can operate in wide temperature range (nothing to freeze, boil, or evaporate)

- can be used in parallel with fuel or solar cells to form hybrid power source, especially suitable for applications requiring pulse power.

Prospects for Future Research

Future work is planned for making nanoporous membranes in alumina and titania with controlled pore diameters from 10 to 300 nm to further test and improve energy density found to date. The advantage of using titania membranes is that the dielectric coefficient of titania is 100, which is 10X higher than that of currently used alumina having the dielectric coefficient of value 9.6. This difference in dielectric coefficients will translate directly to 10X increase in energy density.

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